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# PHOTOIONIZATION AND THRESHOLD PHOTOELECTRON—PHOTOION COINCIDENCE STUDY OF CYCLOPROPENE FROM ONSET TO 20 eV

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## ABSTRACT

The photoionization efficiency curves have been obtained for cyclopropene and its fragments $C_3H_3^+$, $C_3H_2^+$, and $C_3H^+$ from threshold to 20 eV. The threshold photoelectron spectra and breakdown curves are given over the same energy range. The breakdown curve is almost identical to those obtained previously for allene and propyne when put on a common energy scale. This suggests that all three ions isomerize to a common structure before fragmentation.

## INTRODUCTION

This is the fourth in a series of papers from this laboratory dealing with the fragmentation of the $C_3H_4^+$ isomeric system. Previous reports included studies of the fragmentation of allene [1] and propyne [2] ions and an allene ion kinetic study [3]. In this paper data for the last member of the isomeric system, cyclopropene, are reported.

Previous work on cyclopropene includes a study of its photoelectron spectra (PES) by Bischof and Heilbronner [4]. They reported an adiabatic ionization potential (ionization energy) of 9.70 eV. Robin et al. [5], also using photoelectron spectroscopy, reported an adiabatic ionization potential of 9.67 eV along with thresholds corresponding to six other excited states of the ion. The adiabatic first ionization potential agrees well with that determined by Lossing [6] using monoenergetic electron bombardment.

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Lossing [6] also carefully measured the appearance potential (appearance energy) of the $C_3H_3^+$ fragment from cyclopropene parent ions. He reported a value of 10.59 eV for the appearance potential and from this derived a heat of formation ($\Delta H_f$) of 1075 kJ $mol^{-1}$ (257 kcal $mol^{-1}$) for the $C_3H_3^+$ ion. Lossing pointed out that this heat of formation of the $C_3H_3^+$ ion from cyclopropene was approximately the same as that of the $C_3H_3^+$ ion from both allene and propyne. From a separate determination of the heat of formation of the propargyl ion, he concluded that the structure of $C_3H_3^+$ from the above fragmentations was of the cyclopropenyl form. This implies that a rearrangement occurred between the formation of the linear allene or propyne ions and the H-loss fragmentation.

In our previous studies we established that the fragment ions from allene and propyne observed in the energy range from ionization threshold to 20 eV had the same heat of formation. In addition, except for some minor differences, the breakdown curves for allene and propyne, i.e., the relative abundance of fragment ions as a function of parent ion internal energy, were identical. This suggested that the fragmentation proceeded from a common ionic species in both cases and that it yielded the same fragment ion structures throughout the energy range investigated. In the case of allene, Stockbauer and Rosenstock [3] determined that at the threshold for formation of the $C_3H_3^+$ ion the parent ion maintained the allene structure so that H loss from $C_3H_4^+$ and rearrangement to the cyclopropenyl fragment ion occurred as a concerted process.

We have studied cyclopropene using photoionization and threshold photoelectron—photoion coincidence from ionization threshold to 20 eV. This paper reports the photoionization efficiency curves, threshold photoelectron spectra (TPES) and breakdown curves for cyclopropene.

## EXPERIMENTAL

The photoionization experiments, threshold photoelectron and photoelectron—photoion coincidence experiments were performed on the same equipment and in the same manner as for allene and propyne [1,2]. The details of the threshold photoelectron—photoion mass spectrometer have been published elsewhere [1,7,8].

Both instruments utilize the hydrogen many-line spectrum and the Hopfield continuum of helium. The light is dispersed in both instruments with 1-m Seya—Namioka monochromators. Appropriate differential pumping allows for windowless operation.

The photoionization mass spectrometer is a 3-in (7.62-cm) radius-of-curvature magnetic instrument using a channel electron multiplier for ion detection. The light intensity is monitored with a sodium-salicylate-coated photomultiplier which is assumed to have a constant quantum yield.

The threshold photoelectron—photoion coincidence mass spectrometer has a mass resolution of ca. 80 with a nominal energy resolution of ca. 25

meV. Ions coincident with an electron produced with zero kinetic energy are detected with the instrument. The ratio of the number of ions of a particular mass to the total number of coincident ions as a function of photon energy gives the breakdown curves directly.

The sample of cyclopropene was prepared by the procedure outlined by Closs and Krantz [9]. Care was taken to remove the allyl chloride impurity in the cyclopropene during synthesis and as a result only a negligible amount was evident from the mass spectrum of the sample. The sample was stored in a liquid nitrogen refrigerator until used and introduced into the mass spectrometers through an all-glass gas handling system. It was found that exposure to metal surfaces at atmospheric pressures caused a significant dimerization of the sample as had been reported previously [10]. To help purify the sample during the TPES and coincidence studies the liquid sample was maintained at 140 K with a pentane slurry. This had the effect of reducing any possible allyl chloride impurity since it was estimated that at this temperature the vapor pressure of cyclopropene would be at least 10 times greater than that of allyl chloride. An analysis of the mass spectrum showed that the only significant impurities might have been $C_3H_4$ isomers.

Because only small amounts of cyclopropene were available, both the photoionization and the coincidence data were obtained using sample pressures lower than those used for the previous allene and propyne studies. For this reason the statistics for the present data are poorer than those we have published previously on allene and propyne.

## RESULTS AND DISCUSSION

The photoionization efficiency curve for the $C_3H_4^+$ parent ion and the fragment ions $C_3H_3^+$, $C_3H_2^+$ and $C_3H^+$ are shown in Fig. 1 from threshold to 600 Å (20.6 eV). The vertical scale of each of the plots has been adjusted to indicate the measured relative intensity. The abscissa is linear in wavelength (Å) with a non-linear energy scale (eV) shown for convenience and for comparison with the other data. Figure 2(A) gives the TPES of cyclopropene and Figs. 2(B) and 2(C) give the breakdown curves.

### *Photoionization results*

#### *Parent ion $C_3H_4^+$*

The parent ion onset, taken as the midpoint of the first linear portion of the photoionization data in Fig. 1, is 9.67 ± 0.01 eV. Owing to the poor statistics the parent ion data were smoothed with a 3-point box average.

The parent ion data show several steps immediately above the onset, which correspond to the vibrational peaks observed in the PES [5] and the TPES reported here. There are several large oscillations in the data above 10.5 eV which correspond to an excited state of the ion as observed by Robin et al. [5]. The other states observed by Robin et al. and observed in

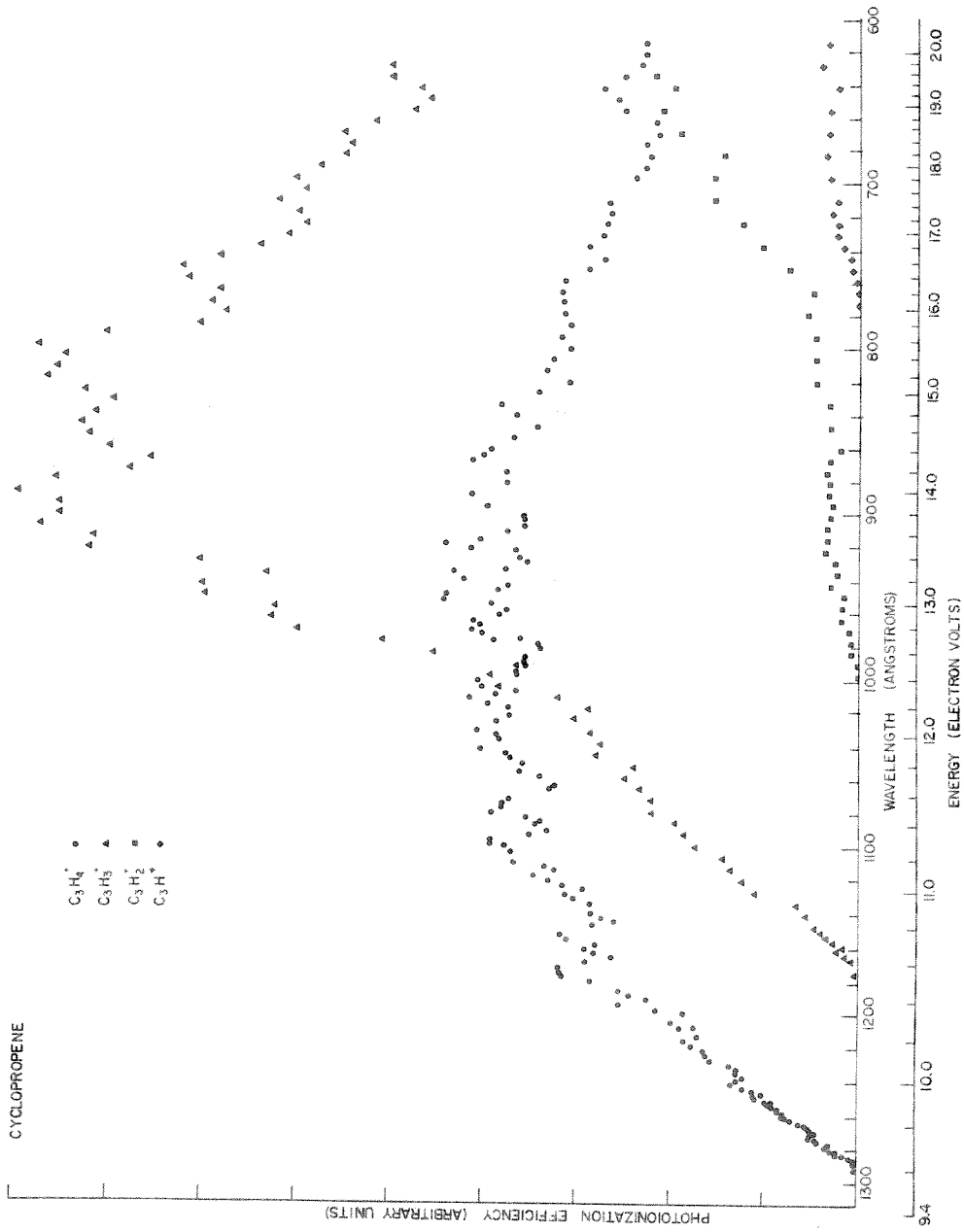


Fig. 1. Photoionization efficiency curve of cyclopropene and its fragment ions between threshold and 600 Å. The ordinate is the photoionization efficiency in arbitrary units. The abscissa is linear in wavelength (Å) with a non-linear energy scale (eV). The data have been corrected to give the correct relative intensities of the parent and fragment ions.

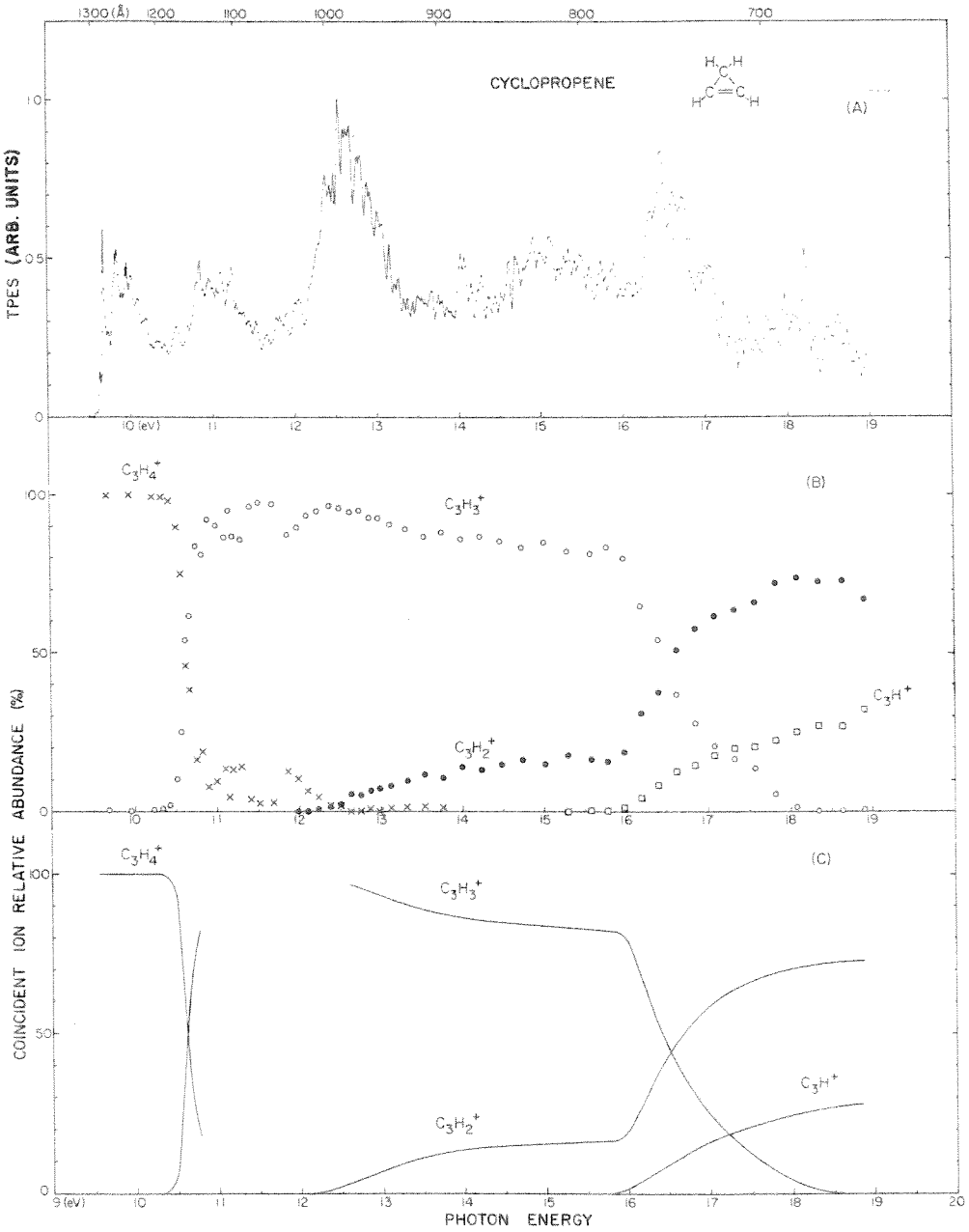


Fig. 2. (A) Threshold photoelectron spectra of cyclopropene from onset to 18.8 eV. The ordinate is electron rate per unit photon in arbitrary units and the abscissa is photon energy (eV) with a non-linear wavelength scale (Å). (B) Breakdown curve for cyclopropene and its fragments. The ordinate is relative coincident ion intensity and the abscissa is photon energy. (C) Breakdown curve for cyclopropene. Same as (B) except for the omission of the pressure-dependent region between 10.8 and 12 eV. A smooth average line has been drawn through the data points.

the TPES do not appear in the photoionization efficiency curve of the parent ion. The parent ion curve remains approximately constant with photon energy, with some structure which may be due to autoionization.

*$C_3H_3^+$ ion*

The appearance potential of the $C_3H_3^+$ fragment ion is 10.59 ± 0.02 eV. The data rise approximately linearly from threshold to about 12.4 eV. At this energy the ion intensity increases much more rapidly, reaching a broad maximum near 14.1 eV. This increase corresponds in energy to a second electronic state of the ion which is observed in the PES and TPES at 12.2 eV. The fact that this state is not observed in the parent ion data suggests that all the ions formed in this electronic state dissociate. At wavelengths shorter than 900 Å the $C_3H_3^+$ data show a gradual decrease, with some structure.

Using the value for the heat of formation of cyclopropene suggested by Rosenstock et al. [11] and ignoring thermal and kinetic shifts, a value of 1079 kJ $mol^{-1}$ (258 kcal $mol^{-1}$) is obtained for the heat of formation of $C_3H_3^+$. The appearance potential of the $C_3H_3^+$ ion as determined by the photoelectron—photoion coincidence measurements is 10.25 ± 0.1 eV. This is lower than the appearance potential given by the photoionization measurements and is due to the different sensitivities and sampling times of the experiments as discussed in refs. 1 and 2.

*$C_3H_2^+$ ion*

The $C_3H_2^+$ ion has an appearance potential of 12.51 ± 0.04 eV as determined by the photoionization technique and 12.15 ± 0.1 eV as determined by the coincidence technique. The $C_3H_2^+$ photoionization efficiency curve in Fig. 1 rises linearly to a maximum at about 12.9 eV. From 13 eV to 16.3 eV the curve is approximately flat. This is presumably due to competition with the process which leads to increased $C_3H_3^+$ formation, which starts at about 12.4 eV. At about 16.3 eV the $C_3H_2^+$ data rise linearly and the ion count reaches an intensity equal to the parent ion intensity at 19.4 eV.

Assuming the reaction leading to the formation of $C_3H_2^+$ at threshold to be

$$C_3H_4 + h\nu \rightarrow C_3H_2^+ + H_2 + e^-$$

the heat of formation of the ion is calculated to be 1481 kJ $mol^{-1}$ (354 kcal $mol^{-1}$) from the photoionization data. This value agrees with the heats of formation for the same ion from allene or propyne parent ions within experimental error.

*$C_3H^+$ ion*

The $C_3H^+$ ion has an appearance potential of 16.3 ± 0.05 eV as measured by the photoionization technique and 15.7 ± 0.1 eV as measured by the coincidence technique. The data in Fig. 1 rise linearly from threshold, reach

a maximum at about 17.2 eV and remain nearly constant above this value. The region where the $C_3H^+$ onset occurs coincides with an excited electronic state of the cyclopropene ion in the TPES and PES at about 16.2 eV.

Assuming the reaction that forms $C_3H^+$ is

$$C_3H_4 + h\nu \rightarrow C_3H^+ + H_2 + H + e^-$$

we obtain a value of 1632 kJ $mol^{-1}$ (390 kcal $mol^{-1}$) for the heat of formation. This value agrees within experimental error with the values obtained for the formation of the same ion from the allene or propyne parent ions.

*Threshold photoelectron spectra*

The TPES data give an adiabatic ionization potential of 9.668 ± 0.005 eV for cyclopropene (taken to be the center of the first large peak). This agrees well with the photoionization value obtained here and those reported from PES [4,5]. The general features of the TPES are also in agreement with the PES [4,5]. Evidence for the excited states observed in the PES are observed in the TPES. The relative intensities are different, but this is understandable in terms of contributions by autoionization and cross-section variations.

The details of the TPES differ from those of the PES in that the TPES shows considerably more structure. Most of this structure is probably due to autoionization processes which produce low-energy electrons. As in allene [1] and propyne [2], these low-energy electron processes allow study of the fragmentation of the parent ion in energy regions not accessible by direct ionization and therefore not accessible with PES.

Table 1 summarizes the appearance potentials of the various ions observed here in both the photoionization and coincidence work and compares the values with those existing in the literature. Table 2 gives the heats of

TABLE 1

Appearance potentials of the cyclopropene ion and its fragments

| Ion | This work | | Other work | | |
|---|---|---|---|---|---|
| | Photoionization (eV) | Coincidence (eV) | Value | Method * | Ref. |
| $C_3H_4^+$ | 9.67 ± 0.01 | 9.668 ± 0.005 | 9.67 | PES | 5 |
| | | | 9.70 | PES | 4 |
| | | | 9.69 | EI | 6 |
| $C_3H_3^+$ | 10.59 ± 0.04 | 10.25 ± 0.1 | 10.59 | EI | 6 |
| $C_3H_2^+$ | 12.51 ± 0.04 | 12.15 ± 0.1 | | | |
| $C_3H^+$ | 16.3 ± 0.05 | 15.7 ± 0.1 | | | |

* PES = photoelectron spectra: EI = electron ionization.

TABLE 2

Heats of formation in kJ $mol^{-1}$ (kcal $mol^{-1}$)

| | Allene * | Propyne ** | Cyclopropene *** |
|---|---|---|---|
| $C_3H_4^+$ | 1126 (269) | 1186 (283) | 1209 (289) |
| $C_3H_3^+$ | 1084 (259) | 1084 (259) | 1079 (258) |
| $C_3H_2^+$ | 1494 (357) | 1505 (360) | 1481 (354) |
| $C_3H^+$ | 1594 (381) | 1620 (387) | 1632 (390) |

* Ref. 1.
** Ref. 2.
*** Present work.

formation of the parent and fragment ions from allene, propyne and cyclopropene [12]. The values for the fragments are those determined here using the photoionization thresholds.

*Breakdown curve*

Figure 2(B) shows the cyclopropene coincidence data, corrected for background, and given in the form of breakdown curves. The data are presented as smooth curves in Fig. 2(C), with the exception of the energy region between 10.9 and 12 eV. In this region the parent ion intensity fluctuated rapidly with photon energy. Since time did not permit a thorough investigation of the pressure dependence of this phenomenon, the region was omitted from the curves in Fig. 2(C).

As in allene and propyne, the only fragmentations observed involve C—H bond ruptures. The first fragmentation observed is H-atom loss, occurring near 10.5 eV. The competitive fragmentation, loss of $H_2$, occurs near 12 eV. Above 16 eV, the secondary processes, loss of H and $H_2$ from the primary fragments, take place to form $C_3H_2^+$ and $C_3H^+$.

## CONCLUSION

The breakdown curve for cyclopropene is very similar to those obtained for allene and propyne and if the energy scales are corrected for the difference in heats of formation of the parent molecules, the three sets of curves coincide fairly accurately.

This suggests strongly that these three parent ions isomerize to a common structure before they fragment. It is surprising that this seems to occur even when nearly 10 eV of internal energy is present in the parent ions.

From the breakdown curves alone we cannot conclude anything about the details of the structure of the common parent ion. However, on inspection of Table 1 we note that $C_3H_4^+$ from both propyne and cyclopropene are metastable in energy with respect to $C_3H_4^+$ from allene. This, combined with the observation of Stockbauer and Rosenstock [3] that the allene ion

retained its structure before the H-loss fragmentation, suggests that the common parent ion has the allene structure.

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